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A METHOD FOR DETERMINING THE QUANTITATIVE CONTENT OF PHASES IN GLASS CERAMICS

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A standard-free x-ray qualitative phase analysis method is proposed for analyzing structural transformations in the course of crystallization and obtaining a quantitative estimate of the content of phases after various heat-treatment and radiation schedules.

It is known that the physicochemical properties of glass ceramics and photoglass ceramics to a great extent depend on the quantitative content of crystalline phases in the material. Therefore, to select optimum conditions for glass crystallization and to control the properties of glass ceramics, it is essential to have a quantitative x-ray method for determining the crystalline and vitreous phases in the microstructure of glass ceramics. However, such a method has not yet been developed. The method proposed by Ohlberg and Strickler [1] is restricted by several assumptions that need to be verified for each glass composition.

It was assumed, for instance, that only the intensity of scattering of x-rays by the vitreous phase changes in the course of crystallization, and the type of diffuse halo of the initial glass does not, whereas it is known that in sodium-bearing partly crystallized glass the intensity distribution of the vitreous phase scattering changes. It was also assumed that the absorption coefficients of the initial glass and the residual vitreous phase in glass ceramics are similar, which appears to be incorrect considering the differences in the chemical compositions of the initial glass and the residual vitreous phase. The method is based on the assumption that the vitreous phase scattering intensity decreases in proportion to the growing quantity of the crystalline phase formed from the amorphous phase. By measuring scattering for a mechanical mixture of crystalline compounds corresponding to the initial glass composition, a correction for scattering in an air medium and Compton scattering was introduced. According to a simplified method [2], measurements are performed for a particular value of the scattering angle 2θ , and the degree of crystallization is calculated from the expression

$$K = 100 \frac{I_g - I_x}{I_g - I_\beta},$$

where K is the volume content of the crystalline phase, %; I_g , I_x , and I_β are the scattering intensities for the amorphous

phases of the initial glass, partly crystallized glass, and a mechanical mixture of crystalline compounds measured for a certain value of the scattering angle 2θ .

We have proposed a standard-free x-ray method for quantitative phase analysis to study structural transformations in crystallization and to determine the quantitative content of the phases after various regimes of heat treatment and radiation. This method is applicable only to multiphase crystalline materials in which the mass absorption coefficients of the crystalline phases differ insignificantly and have an approximately equal scattering capacity. The method proposed was first tested to determine the quantitative content of crystal phases in the products of crystallization of lithium-aluminosilicate light-sensitive glasses, in which the main crystalline phases are lithium meta- and disilicate, β -eucryptite, and β -spodumene, as well as their solid solutions. Calculations demonstrated that the mass absorption coefficients of these crystalline phases in copper CuK_α radiation differ insignificantly. Thus, the mass absorption coefficient of lithium meta- and disilicate is equal to $36 \text{ cm}^2/\text{g}$ and that of β -eucryptite and β -spodumene is equal to $39 \text{ cm}^2/\text{g}$.

The main scattering elements in the crystalline phases considered are Si^{4+} , Al^{3+} , and O^{2-} ions, whose scattering capacity according to the available published data [3] shown in Fig. 1 is virtually equal in the intervals of x-ray scattering angles for photoglass ceramics. The scattering capacity of Li^+ ion for the specified crystalline phases can be neglected.

The method is based on the conservation law for the integral x-ray scattering intensity [4, 5]. The intensity conservation law states that the intensity is determined by the volume integral of the electron density squared of the scattering object:

$$\int I(S) dV_s = \int \rho^2(r) dV_r,$$

where $I(S)$ is the scattering intensity of x-rays in the inverse space; S is the inverse lattice vector; $S = 4\pi \sin \theta / \lambda$

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($\lambda = 1.54 \text{ \AA}$ is the x-radiation wavelength); dV_s is the elementary volume in the reverse space; $\rho^2(r)$ is the mean electron density of the crystalline and the vitreous phases in the sample considered; dV_r is the elementary volume in direct space.

Assuming the mean electron density of the crystalline and the vitreous phases to be approximately equal, the scattering intensity of the crystalline phases to be concentrated in the reflections, and that of the vitreous phase in the diffuse halo, they can be distinguished in the diffraction patterns. Next, in performing quantitative x-ray phase analysis, the integral scattering intensity of each crystalline and vitreous phase can be measured. On performing such measurements, one can determine the volume content (%) of phases in the heterogeneous system, i.e., the glass-ceramic material, using the following formula:

$$I_{1k} + I_{2k} + \dots + I_{am} = 1,$$

where I_k is the integral intensity of the k th crystalline phase and I_{am} is the integral scattering intensity of the vitreous phase of the sample.

An example of a separation of scattered x-radiation on the diffraction pattern of a photoglass-ceramic material is shown in Fig. 2. Having eliminated the incoherent Compton scattering [5] and scattering in the air medium from the curve and taking into account the law of conservation of integral intensity, one can write:

$$\int (I_{am} + I_{cr}) dV_s = \rho_m^2 \int (dV_{am} + dV_{cr}), \quad (1)$$

where ρ_m^2 is the square of the electron density of the crystalline and the vitreous phases in the sample, if the scattering intensity distribution is spherically symmetric, i.e., assuming that the orientation of the crystallographic axes in the samples is isotropic. In this case formula (1) takes the form

$$\int I_{cr}(S) \times 4\pi S^2 dS = \rho_m^2 \int dV_{cr}; \quad (2)$$

$$\int I_{am}(S) \times 4\pi S^2 dS = \rho_m^2 \int dV_{am}. \quad (3)$$

A method for determining the degree of crystallization (vol.%) based on diffraction patterns was proposed in [4], where approximated relationships were used:

$$\int I_{cr}(S) dS \approx \rho_m^2 \int I_{cr}(\theta) d\theta \sim K_{cr}; \quad (4)$$

$$\int I_{am}(S) dS \approx \rho_m^2 \int I_{am}(\theta) d\theta \sim K_{am}, \quad (5)$$

so that $K_{cr1} + K_{cr2} + K_{cr3} + \dots + K_{am} = 1$.

A comparison of formulas (4) and (5) with formulas (2) and (3) shows that formulas (4) and (5) are incorrect, but they can give a result close to the true one if I_{cr} and I_{am} are approximately equally distributed over the values $S = 4\pi \sin \theta / \lambda$. In this case the factor $4\pi S^2$ will not modify the ratio $K_{cr} : K_{am}$.

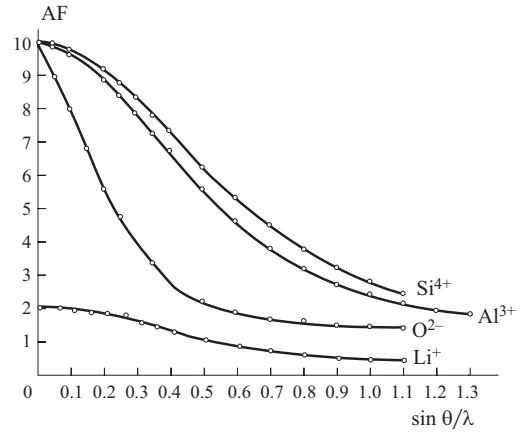


Fig. 1. Dependence of atomic scattering factor (AF) of x-ray scattering by Si^{4+} , Al^{3+} , O^{2-} , and Li^{+} ions on the inverse lattice vector $\sin \theta / \lambda$.

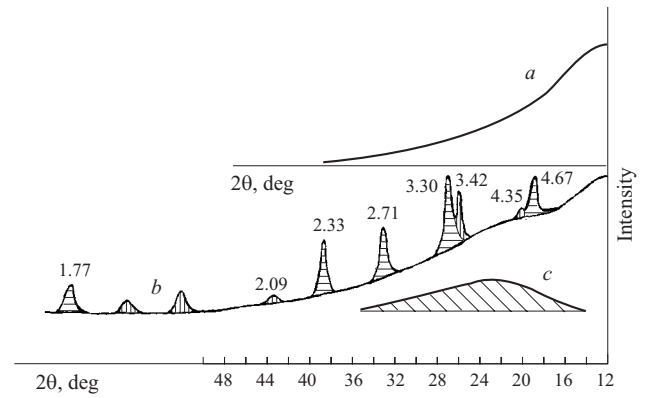


Fig. 2. Diffraction pattern of photoglass-ceramic sample: a) curve of scattering in air medium; b) diffraction pattern of the sample; c) amorphous halo; (▨) lithium metasilicate, (▩) β -eucryptite solid solution.

Thus, interference only modifies the spatial distribution of diffracted x-radiation without changing its mean intensity, which does not depend on the position of atoms and ions and is equal to the intensity created by the same number of atoms scattering x-rays independently of each other. The phrasing of the law of conservation of intensity recalls the known law of conservation of energy.

The method described above was used to study lithium-aluminosilicate photoglass ceramics containing several crystalline phases. X-ray diffraction of photoglass-ceramic samples was carried out on a DRON-1 x-ray set with $\text{CuK}\alpha$ radiation and a β -filter. The experimental determination of integral intensity was reduced to measuring the surface areas of the diffraction peaks of all crystalline phases, as well as that of the sought for crystalline phase and the surface area of the amorphous halo constructed in the coordinates $I(2\theta) - 2\theta$.

The intensity distribution in the diffraction lines was recorded on a strip-chart recorder. To perform a quantitative phase analysis, it is necessary to measure precisely the dif-

TABLE 1

Sample	Photoglass ceramics with different contents of R ₂ O and RO, %	Molar content of R ₂ O and RO, %	Content of crystalline phase, vol.%				Total content of crystalline phases, vol.%	TCLE, 10 ⁻⁷ K ⁻¹ in temperature interval 20 – 300°C
			Li ₂ O · SiO ₂	Li ₂ O · 2SiO ₂	β-eucryptite solid solution	α-eucryptite		
1	N-2	1 Na ₂ O	18	20	50	—	90	84.5
2	N-3	2 Na ₂ O	18	15	15	—	50	92.3
3	K-4	2 K ₂ O	28	7	23	—	70	147.3
4	L-2	26 Li ₂ O	54	17	—	—	70	145.3
5	KN-2	2 K ₂ O 2 Na ₂ O	35	—	—	—	40	93.7
6	S-1	0 SrO	51	—	25	5	80	—
7	S-11	10 SrO	36	5	—	5	40	100.5
8	BA-1	0 BaO	54	5	14	7	80	92.0
9	BA-2	1 BaO	47	5	8	25	80	79.0
10	BA-3	2 BaO	42	5	5	29	80	89.0

fraction maximum intensities. According to the data in [6], the requirement of high accuracy and sensitivity in determining the line intensities is related to using wide slots intensifying the luminosity of the diffractometer, large time constants, and, accordingly, low velocities of the counter to decrease the statistic fluctuations of the count.

The rotational speed of the counter in determining the content of the crystalline phases was 0.5 deg/min, and the velocity of the strip-chart velocity was 2400 mm/h. To raise the integral intensity, slots (2; 2; 0.25 mm) intensifying the luminosity of the diffractometer were used. This selection of experimental conditions makes it possible to determine the integral intensity accurately enough.

The areas of the peaks on the diffraction patterns were measured using a PP-2K (NIIZ) planimeter. According to our results, the precision of determining the content of the crystalline and the amorphous phases is limited by the accuracy of measuring the integral intensity and is approximately 5%.

The experimental verification of the method was performed on photoglass-ceramic samples of the lithium-aluminosilicate system with different contents of Na₂O, K₂O, Li₂O, SrO, and BaO. The results of determination are shown in Fig. 2 and in Table 1, in which the TCLEs of the photoglass ceramics considered are listed as well.

It can be seen that the TCLE of lithium-aluminosilicate photoglass ceramics of different chemical compositions agrees with its content of crystalline phases and depends on the total quantity of the crystalline and the vitreous phases. The minimum TCLE values within the limits of $(84.5 - 92.3) \times 10^{-7} \text{ K}^{-1}$ were registered in samples 2 and 3 with the maximum content of quartz-like solid solution of β-eucryptite (15 – 20%), which is known to have a minimum value of thermal expansion [2].

The maximum TCLE values varying from 93×10^{-7} to $145 \times 10^{-7} \text{ K}^{-1}$ were seen in photoglass-ceramics KN-2, L-2, S-1, S-11, BA-1, and BA-2, in which the solid solution of β-eucryptite either was totally absent, or its content was

5 – 8%. The prevailing crystalline phases in these photoglass-ceramics were lithium meta- and disilicate that have a high TCLE, namely 195×10^{-7} and $100 \times 10^{-7} \text{ K}^{-1}$, respectively. A substantial TCLE ($143 \times 10^{-7} \text{ K}^{-1}$) registered in photoglass ceramic K-4 with 23% solid solution of β-eucryptite can be attributed to the presence of a large quantity of lithium metasilicate (28% compared to 18% in samples 2 and 3), as well as by a probably modification in the composition of β-eucryptite solid solution, which leads to a higher TCLE.

Thus, a reference-free quantitative x-ray method is proposed for determining the content of crystalline phases in glass ceramics.

A theoretical substantiation of the method is given, together with the results of an experimental quantitative determination of each crystalline phase in the products of crystallization of lithium-aluminosilicate light-sensitive glasses with different quantities of Na₂O, K₂O, Li₂O, SrO, and BaO additives.

A correlation between the content of these phases and the TCLE of crystallized glasses with different R₂O contents is established.

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